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Synthesis and Characterization of Polyaniline – Carbon Nanotube and Nanofibre Composites

Preliminary Experiments

D.A. Makeiff
M.N. Diep
M.C. Kopac
T.A. Huber

Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2005-156
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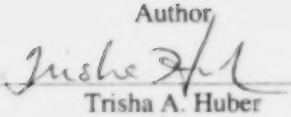

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Abstract

There is significant interest in new materials exhibiting favourable electronic properties, such as carbon nanotubes and conducting polymers. Both have been discovered relatively recently, and have attracted great interest from the research community due to their exceptional properties, as well as their versatility in terms of tailoring these properties. Particular interest stems from the idea that a combination of these two species may give rise to a composite possessing properties that are superior to the parent components, and exhibit a synergy in terms of electrical properties. We have prepared polyaniline – carbon nanotube and polyaniline – carbon nanofibre composites under a variety of reaction conditions, and have characterized the products using electron microscopy (scanning and transmission) and DC conductivity. The results of our preliminary experiments are presented here.

Résumé

Les nouveaux matériaux possédant des propriétés électroniques intéressantes, comme les nanotubes de carbone et les polymères conducteurs, suscitent un intérêt considérable. À cause de propriétés exceptionnelles et la facilité avec laquelle on peut les adapter à différents usages, ces deux familles de matériaux récemment découvertes ont attiré l'attention de la communauté des chercheurs. On retient particulièrement la possibilité de produire, en combinant ces deux espèces, un composite aux propriétés qui leur seraient supérieures, notamment les propriétés électriques résultant de la synergie. Nous avons élaboré, sous diverses conditions de réaction, des composites de nanotubes de carbone et de polyaniline, ainsi que de nanofibres de carbone et de polyaniline, et nous avons caractérisé leur conductivité en courant continu et par microscopie électronique (en transmission et par balayage). Nous présentons les résultats de nos premières expériences.

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Executive summary

Introduction

Carbon nanotubes are very long (typically up to hundreds of microns), very thin (typically less than 20 nanometers) tubes of carbon that are produced as either single-walled nanotubes (SWNT) or multi-walled nanotubes (MWNT). They derive their exceptional mechanical, electrical, and thermal properties from both their high aspect ratio (ratio of length to diameter), as well as their conjugated π system. Conducting polymers are polymers that possess a conjugated π system, and are rendered electrically conductive upon reduction or oxidation of the conjugated π electrons. A composite derived from both species promises to yield interesting properties as the nanotubes and conducting polymers complement each other well in terms of mechanical integrity and wettability. Moreover, nanotubes have been found to interact with other conjugated species, thus electronic interaction is possible between nanotubes and conducting polymers. In fact, there are reports in the literature of such composites exhibiting enhanced conductivity (composite conductivity exceeds that of the component materials).

Results

The synthesis of polyaniline in the presence of dispersed carbon nanotubes and nanofibres yields polymer coated carbon nanostructures, as evidenced by electron microscopy (both scanning and transmission). The coating thickness and presence of polyaniline nanoparticles or nanotubules is dependent on the reaction conditions. The DC conductivity data indicate that the composite exhibits enhanced conductivity relative to the bulk parent materials, although it is difficult to distinguish enhancement due to true contact resistance from that resulting from packing effects.

Significance

The existence of a conductivity enhancement, in addition to improvement in environmental stability and mechanical properties, yields a composite that is superior to the individual components. In addition, the improvement in capacitance, as reported in the literature, indicates that such a composite holds great promise as a supercapacitor, which would be of great interest for the military for lightweight energy storage purposes. Furthermore, such a composite would also be of military, as well as commercial interest, for other applications that currently use conventional electrically conducting species (electrical components, displays, rechargeable batteries, sensors, etc.).

Future plans

As mentioned previously, these results are preliminary and a great deal of experimentation is planned, including more rigorous investigation into nanotube dispersion and the assessment of nanotube surface functionality. Correlating reaction conditions with coating thickness (assessed by high resolution transmission electron microscopy, HRTEM) and DC

conductivity will be undertaken. In addition, spectrocopy will be utilized to probe the degree of electronic interaction between the nanotubes and polyaniline. Lastly, composites prepared from polyaniline derivatives and/or surface-functionalized nanotubes will be studied, and their structure-property relationships elucidated.

D.A. Makeiff, M.N. Diep, M.C. Kopac, T.A. Huber; 2005; Synthesis and Characterization of Polyaniline – Carbon Nanotube and Nanofibre Composites; DRDC Atlantic TM 2005-156; Defence R&D Canada – Atlantic.

Sommaire

Introduction

Les nanotubes de carbone sont des cylindres de carbone, très longs (quelques centaines de micromètres habituellement), très minces (moins de 20 nanomètres en général) et présentant une paroi simple ou des parois multiples. Leurs exceptionnelles propriétés mécaniques, électriques et thermiques résultent de leur rapport de forme (ratio longueur-diamètre) et de leur système de conjugaison des électrons π. Les polymères conducteurs possèdent également un système de conjugaison d'électrons π et peuvent conduire l'électricité à la suite de l'oxydation ou la réduction des électrons π conjugés. Les matériaux composites formés de nanotubes et de polymères conducteurs pourraient présenter des propriétés intéressantes, puisque ces deux espèces chimiques sont complémentaires du point de vue de l'intégrité mécanique et de la mouillabilité. En outre, l'on a découvert que, puisque les nanotubes pouvaient interagir avec d'autres espèces possédant une structure de conjugaison, il était possible d'obtenir une interaction électronique entre les nanotubes et les polymères conducteurs. De fait, des articles scientifiques signalent l'existence de tels composites qui présentent une conductibilité améliorée (leur conductivité globale surpassant celle des composés originaux).

Résultats

La synthèse de polyaniline dans une dispersion de nanotubes et de nanofibres de carbone produit des nanostructures de carbone recouvertes de polymère que l'on peut observer en microscopie électronique (en transmission ou par balayage). Les conditions de réaction déterminent l'épaisseur du revêtement et la formation de nanoparticules ou de nanotubules de polyaniline. Les données de conductivité en courant continu indiquent que la conductibilité des composites dépasse celle des matériaux originaux, bien qu'il soit difficile de distinguer cette amélioration, étant donné la résistance réelle de contact découlant des effets de tassement.

Portée

La conductibilité accrue, en plus de l'amélioration de la stabilité face aux influences externes et des propriétés mécaniques, fait de ces composites des matériaux supérieurs aux composés d'origine. En outre, l'amélioration de la capacitance, signalée dans les écrits scientifiques indique qu'un tel composite pourrait permettre l'élaboration de super-condensateurs. Un tel dispositif de faible masse permettant de stocker de l'énergie serait d'un grand intérêt militaire. Outre son importance militaire, l'utilisation de ce composite dans des appareils utilisant des composantes traditionnelles pour le transport d'électricité (composantes électriques, affichages, piles rechargeables, capteurs, etc.) présenterait un intérêt commercial.

Futures recherches

Comme nous le mentionnions plus haut, nos résultats sont préliminaires et beaucoup d'autres expériences sont prévues, notamment une recherche plus rigoureuse de la dispersion des nanotubes et l'évaluation de la fonctionnalité de la surface des nanotubes. Nous entreprendrons l'étude de la corrélation entre la conductibilité du courant continu et l'épaisseur du revêtement (évaluée par microscopie électronique par transmission à haute résolution). En outre, nous sonderons, par spectroscopie, le degré d'interaction électronique entre les nanotubes et la polyaniline. Finalement, nous étudierons les composites élaborés à partir de dérivés de la polyaniline ou de nanotubes fonctionnalisés en surface, et nous éluciderons les relations entre la structure et les propriétés.

D.A. Makeiff, M.N. Diep, M.C. Kopac, T.A. Huber; 2005; Synthesis and Characterization of Polyaniline – Carbon Nanotube and Nanofibre Composites; DRDC Atlantic TM 2005-156; Defence R&D Canada – Atlantic.

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1. Introduction

The last few decades have witnessed the emergence of a number of interesting electronic materials including conducting polymers and carbon nanotubes. There is great interest in these novel materials, both for substitution of metallic materials in conventional applications, as well as emerging technologies poised to exploit their exceptional properties. Potential (and in some cases realized) applications of carbon nanotubes include electrodes, sensors, electromagnetic shielding and absorption devices, actuators (such as artificial muscles), drug delivery systems, electronic devices (such as transistors), display components (electron field emitters), energy storage (capacitors, fuel cell components), as well as nanotubes as reinforcing and/or thermally conductive fillers. This list is not exhaustive and we can expect to see additional emerging technologies based on these materials.

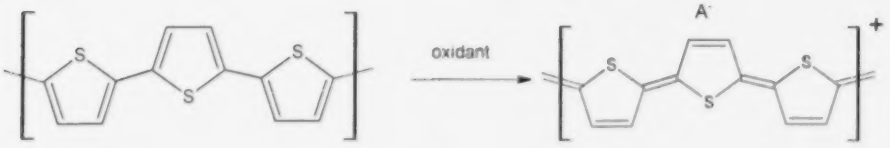
There are a number of reports in the literature of conducting polymer – carbon nanotube composites; since 1999, over 20 papers have been published on polyaniline – carbon nanotube composites alone.[1-23] There are also many reports on carbon nanotube composites with polyaniline derivatives,[24,25] polypyrrole,[26-30] and polythiophene derivatives.[27,31-37] Such conducting polymer – carbon nanotube (CP-NT) composites are particularly interesting as both components are electrically conductive as a direct result of possessing a conjugated π system. Many speculate that an electronic interaction, or synergy, should exist between carbon nanotubes and conducting polymers. In fact, the conjugated π system of carbon nanotubes, which may be envisioned as rolled up sheets of graphite, has been found to interact, in a noncovalent fashion, with other species that possess a conjugated π system. The nature of this interaction is believed to be π - π stacking, in which overlap of the π electron wavefunctions of the two species occurs. Presumably, this interaction enables relatively facile charge transport from one species to another. In the composites in question, the conducting polymer may offer a lower energy charge transport path from one nanotube to another, thereby reducing the effective contact resistance between nanotubes.

Although experimentation indicates the existence of such an interaction in many cases,[1,10,13,22,31] other researchers have found no evidence for interaction.[4,6,19,29,37] This apparent discrepancy is likely a result of differing starting materials, or preparative methods, resulting in varying degrees of conducting polymer conductivity or carbon nanotube-conducting polymer interaction (*vide infra*). Inspection of the literature reveals a wide variety of methods used to produce polyaniline – carbon nanotube composites. The methods employed range from *in-situ* polymerization,[1,2,24] where polymerization of the monomer takes place in the presence of the nanotubes, to simple blending[2,3] (also known as *ex-situ* polymerization), where the ready-made polymer is mixed with the nanotubes. Composites involving both single-walled nanotubes (SWNT)[2,3] and multi-walled nanotubes (MWNT)[1,24] have been prepared, and most researchers utilize *in-situ* polymerization, either chemical or electrochemical, to prepare composites in which the resulting polyaniline is in the doped form.

Conducting polymers, in their neutral or undoped state, are electrically insulating. Their conductivity arises from a process known as doping, and results from the formation of a charged backbone, usually positive. For both polypyrrole and polythiophene, doping is commonly accomplished by the oxidation (removal) of electrons from the conjugated π

system (see Figure 1). For polyaniline, the doping method typically involves the protonation of imine nitrogen atoms that form part of the backbone (see Figure 2). In any case, doping results in the introduction of charge carriers and energetically accessible states within the band gap, E_g, of the conducting polymer, rendering the polymer conductive. Increases in conductivity of 10 – 11 orders of magnitude may be realized, given appropriate preparation and doping conditions.

Polypyrrole



Polythiophene

Figure 1. *Neutral and Doped Polypyrrole and Polythiophene*

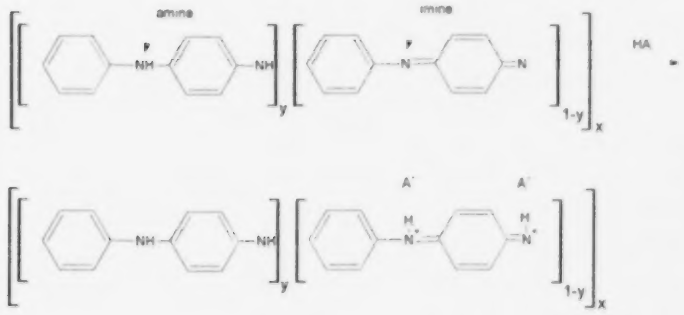


Figure 2. *Neutral and Doped Polyaniline*

There are a number of reasons why discrepancies might exist in the reported results, including varying preparative method, condition of the starting nanotubes, and the degree of dispersion of the nanotubes. In many of the composites in which an electronic interaction was not observed, the conducting polymer is either not doped or only very slightly doped. If the polyaniline is not sufficiently doped, then any coating on the nanotubes will be insulating, and

no reduction in contact resistance should be expected. Although carbon nanotubes are known to be good electron acceptors, and conducting polymers, being relatively easily oxidized, would be considered good electron donors, any doping effect the nanotubes might have on the polymer would be fairly minimal, resulting in a small number of charge carriers. Furthermore, in many cases where conductivity enhancement was not observed, the composite was prepared by simply mixing conducting polymer and carbon nanotubes together (*ex-situ* polymerization). Studies have shown this to be a much less effective method compared to *in-situ* polymerization,[19] presumably due to less intimate electrical contact resulting from the obvious issues associated with mixing long polymeric chains and high aspect ratio species. Variation in results can also be expected given the range of nanotubes employed; differences in the nanotubes and their ease of dispersion and composite formation depends on the type (SWNT or MWNT), preparative method (resulting in differences in aspect ratio ranges), degree of purity (presence of catalyst particles and amorphous carbon), as well as surface functionalization, or degree of graphitization. In addition, the degree of effort expended in dispersing the nanotubes will have an effect on the electrical properties of the resulting composite; poorly dispersed nanotubes will not give rise to uniformly polymer-coated nanotubes, thus any contact resistance reduction will be inhomogeneous. One of the most critical aspects of preparing composites with carbon nanotubes is the dispersion of the tubes in the matrix polymer. In the case of conducting polymers, where the goal is to coat the tubes, effective dispersion is critical for formation of a uniform polymeric coating of the polymer.

There is significant interest in assessing the degree of electronic interaction between conducting polymers and carbon nanotubes, and investigating a means of optimizing the interaction. Enhanced interaction would likely yield improvements in the performance of such composites in applications that rely on the electrical conductivity. Indeed, there is evidence that polypyrrole-MWNT composites exhibit greater capacitance than either polypyrrole or MWNTs alone.[30]

In an effort to assess the presence of electronic interaction, we have prepared several polyaniline – carbon multi-walled nanotube (PAni-NT) and polyaniline – carbon nanofibre (PAni-CNF) composites by *in-situ* polymerization, and report here preliminary results of DC conductivity and electron microscopy studies. The basis for this technical memorandum is a paper presented at Nanotube 2004.

2. Experimental

Aniline (Aldrich, > 99.5%) was distilled under vacuum before use. *p*-toluenesulfonic acid (PTSA) (Aldrich, 98 %), dodecylbenzenesulfonic acid (DBSA) (Aldrich, 70 wt% solution in 2-propanol), multi-walled nanotubes (MWNT) (Aldrich, > 95%, d = 20 - 50 nm, l = 5 - 20 μm), toluene (Aldrich, > 99.5 %), and ammonium persulfate (APS) (Fisher Scientific, 99%) were used as received. The carbon nanofibers (Pyrograf III carbon fibers, grade PR-24-PS-LD) were ball-milled before use.

Unless stated otherwise, the composites were prepared by chemically polymerizing aniline in the presence of dispersed nanotubes (*in-situ* polymerization). The oxidant:monomer ratio was 1:1 for the *p*-toluenesulfonic acid (PTSA) experiments, and 3:4 for the dodecylbenzenesulfonic acid (DBSA) experiments.

Samples for electrical conductivity measurement were prepared by grinding the bulk powder with a mortar and pestle, then pressing pellets (13 mm in diameter, ~ 1 mm thick) under 10 tons of pressure. The conductivity was measured using the standard four-point-probe method, in which 4 equally spaced in-line metal probes (Jandel Scientific, tungsten carbide probes spaced 1.00 mm apart) are placed in contact with the pellet; a current is applied to the outer two probes (Fluke 8000A Digital Multimeter), while the voltage drop is measured between the inner two probes (Hewlett Packard 34401A Multimeter). The resistivity (thus the conductivity) is determined from the current-voltage data, and the sample dimensions.

SEM samples were typically prepared as follows: the product was dispersed *via* sonication in ethanol, then one drop of the dispersion was applied to a carbon or aluminum stub, followed by sputter-coating with gold. SEM images were acquired using a Jeol LEO 1455VP scanning electron microscope. TEM samples were prepared by dropping an ethanol suspension of product (dispersed *via* sonication) onto holey carbon supported by a copper grid. TEM images were acquired on a Hitachi H-7000 transmission electron microscope.

2.1 PAni/PTSA Carbon Nanostructures

2.1.1 –PAni/PTSA-MWNT (in ethanol)

Typically, 30 – 100 mg nanotubes were sonicated (12 W/55 kHz, or 100 W/47 kHz) for approximately 5 minutes in 30 mL of an ethanol solution containing 0.84 M *p*-toluenesulfonic acid (PTSA) and 0.055 M aniline, followed by cooling to ~ 0°C. A precooled 5 mL solution of 0.32 M ammonium persulfate (APS) in a 3:2 mixture (by volume) of ethanol:water was added. The reactions were carried out at lower temperatures (0 – 5 °C), and the reaction was allowed to proceed overnight. The product was isolated by vacuum filtration through a medium sintered glass frit. The isolated product was washed with ethanol and acetone, and dried *in vacuo*. After drying, conductivity measurements were performed on pressed pellets of the ball-milled product.

2.1.2 PAni/PTSA-CNF (in ethanol)

The *p*-toluenesulfonic acid doped polyaniline – carbon nanofibre composites (PAni/PTSA-CNF) were prepared by the same method as for PAni/PTSA-MWNT, and characterized by SEM, TEM, and DC conductivity.

2.2 PAni/DBSA-Carbon Nanostructures

2.2.1 PAni/DBSA-MWNT

The dodecylbenzenesulfonic acid doped polyaniline – MWNT (PAni/DBSA/MWNT) composites were prepared by *in-situ* polymerization in both toluene and ethanol. For the composites prepared in toluene, a solid was isolated from the dark green reaction mixture, in which PAni/DBSA is soluble to a certain degree. This method was employed in an attempt to selectively polymerize aniline on the surface of the nanotubes, as opposed to precipitating already formed polyaniline onto the nanotubes. Polyaniline that has formed preferentially on the nanotube surface should exhibit maximal electronic interaction with the nanotubes. To accomplish this, the reactant concentrations were fairly dilute in order to encourage solubility of the bulk polymer (not that formed on the nanotube surface) in the solvent.

2.2.1.1 PAni/DBSA-MWNT (in toluene)

Approximately 50 mg nanotubes were dispersed in toluene containing 0.50 mL aniline *via* high frequency, low power sonication (12W, 55kHz) for approximately two hours. 0.94 g APS was dissolved in ~ 10 mL of water and slowly added dropwise to the toluene suspension with stirring. After addition was complete the reaction was allowed to stir overnight to ensure completion of reaction. The reaction mixture was transferred to a separatory funnel, and the organic layer was washed twice with ~ 20 mL of a 1:1 acetone:water mixture in order to remove excess DBSA and reaction by-products. The organic layer (which contains the nanostructures and PAni/DBSA) was filtered through a track-etched polycarbonate membrane (Millipore, 0.2 micron diameter pores) to collect the solid. The solid was then washed with ethanol, and dried *in vacuo* at room temperature for at least 24 hours. After drying, conductivity measurements were performed on pressed pellets of the product.

2.2.1.2 PAni/DBSA-MWNT (in ethanol)

Typically, 50 mg nanotubes were dispersed in 100 mL ethanol *via* high frequency, low power sonication (12W, 55kHz), for 15 minutes, followed by addition of 0.50 mL aniline, and sonication for an additional 15 minutes. 7.7 mL DBSA solution (70 wt% in 2-propanol) was added, and sonication was continued for 30 minutes (total sonication time 1h). After allowing the mixture to cool to RT, 0.95 g APS in 10 mL of distilled water was added dropwise, with stirring. The reaction was allowed to proceed at RT overnight. The reaction mixture was then filtered through a fine sintered glass frit, and the isolated solid was washed with ethanol. After drying *in vacuo*, conductivity measurements were performed on pressed pellets of the product.

2.2.2 PAni/DBSA-CNF (in toluene)

Typically, 25 – 400 mg carbon nanofibres (CNF) were dispersed in 100 mL toluene containing 2.88 mL DBSA solution (70 wt% in 2-propanol) and 0.50 mL aniline, by sonication (12W, 55kHz) for 2 hours. 0.94 g APS was dissolved in ~ 10 mL of water and slowly added dropwise to the toluene suspension with stirring. After addition was complete the reaction was allowed to stir overnight to ensure completion of reaction. The reaction mixture was transferred to a separatory funnel, and the organic layer was washed twice with ~ 20 mL of a 1:1 acetone:water mixture in order to remove excess DBSA and reaction by-products. The organic layer (which contains the nanostructures and PAni/DBSA) was isolated and the solvent was allowed to evaporate. The solid was then washed with ethanol, and dried *in vacuo* at room temperature for at least 24 hours. After drying, conductivity measurements were performed on pressed pellets of the product.

3. Results and Discussion

3.1 PAni/PTSA Carbon Nanostructures

Composites of *p*-toluenesulfonic acid doped polyaniline (PAni/PTSA) and carbon nanostuctures (both multi-walled nanotubes (MWNT) and nanofibres (CNF)) were prepared by *in-situ* polymerization in ethanol, and characterized by electron microscopy and DC conductivity.

3.1.1 PAni/PTSA-MWNT (in ethanol)

SEM images of the as-received MWNT and the resulting composite, PAni/PTSA-MWNT, are shown in Figure 3. The as-received MWNT exist as entangled mats of variable diameter nanotubes. The SEM image of the composite indicates that the nanotubes are thicker, providing evidence for coating. In other SEM images (not shown), polyaniline particles are also evident, indicating that not all of the polyaniline has preferentially formed on the nanotubes.

TEM images of as-received MWNT and one composite tube are shown in Figure 4. The image of the as-received nanotubes exhibits dark spots, which result from diffraction effects attributed to the crystalline nature of the high quality tubes (highly graphitic). The image of the composite tube shows a fairly thick, rough coating of polymer on the nanotube, as well as polyaniline particles adhered to the coating surface. The thickness of the coating has not been quantified precisely, but appears to be approximately 75% of the diameter of this particular nanotube. Investigations into controlling, and accurately measuring the coating thickness, and its effect on the conductivity will be underway in the future.

The conductivity of the composite, as well as the MWNT and polyaniline, in the form of pellets, was determined using the four-point probe method. The samples were ball-milled for ~ 30 minutes prior to pellet pressing, in order to yield pellets with enough mechanical integrity to allow for conductivity measurement. The density of each pellet was determined using the average pellet thickness, pellet mass, and diameter. A plot of DC conductivity and density as a function of weight % MWNT in the composite is shown in Figure 5. The DC conductivity was observed to increase fairly linearly as the weight % of MWNT in the composite increased. This is in direct contrast to the percolation behaviour exhibited by nanotubes dispersed in an insulating matrix, in which a dramatic increase in conductivity, typically several orders of magnitude, is observed when the percolation threshold is reached. The polyaniline prepared in the absence of the nanotubes exhibited a conductivity of ~ 2.6 S/cm, whereas the conductivity exhibited by the bulk nanotubes was approximately an order of magnitude greater, 24 S/cm. It is important to note that the DC conductivity of pressed pellets of the MWNT, i.e. bulk nanotubes, is significantly lower than the extraordinary conductivity along a given nanotube (10^3 – 10^4 S/cm[38]), due to contact resistance between nanotubes. As shown in Figure 3, the composite conductivity increases with increasing MWNT content. It is particularly interesting to note that the conductivity of the composite was found to exceed that of the bulk nanotubes, when the MWNT loading was greater than ~ 25 weight %. This conductivity enhancement is believed to result from the formation of a

more efficient conductive network, and there are at least two contributing factors: a reduction in the contact resistance between the highly conductive nanotubes resulting from the conductive polyaniline coating, and packing effects that reduce unoccupied space and increase contact points. The composites exhibit fairly high density, even when composed largely of MWNT. This increase in density is likely due to the presence of polyaniline nanoparticles that are pliable, and can easily fill voids. Although these results are preliminary, and replicate experiments should be performed, the trend of increasing conductivity with MWNT loading is clear.

There are a number of reports in the literature of electronic interaction between carbon nanotubes and other species possessing a π system. The nature of the interaction is proposed to be pi-π stacking. Presumably charge transport is occurring through overlap of electronic wavefunctions. In addition, there are reports of interaction between amines, or other nitrogen-containing species, and carbon nanotubes. Polyaniline possesses both a conjugated π system, as well as nitrogen atoms, thus may be well suited for electronic interaction with carbon nanotubes. Although the DC conductivity of the bulk polyaniline is not as high as that of the nanotubes, it is also possible that the assembly of polyaniline on the surface of the nanotubes results in a more ordered polyaniline that is more conductive than that produced in the absence of the nanotubes. This is not unprecedented, as tubes of polyaniline produced by a template synthesis method have been found to be more ordered, and exhibit higher conductivity.[39]

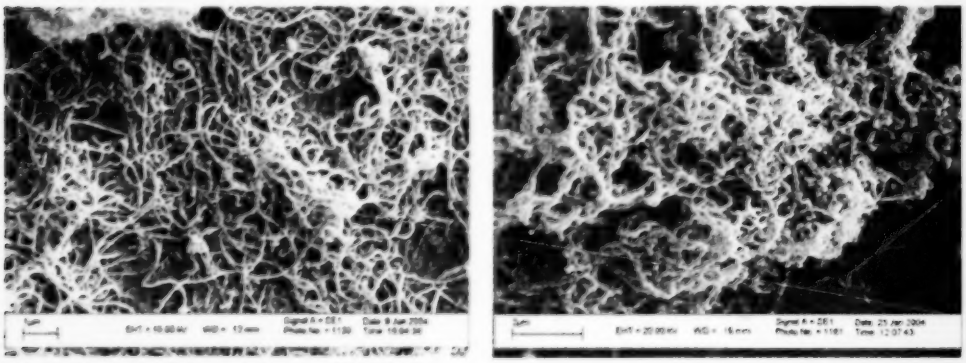


Figure 3. *SEM images of a) MWNT (as received), and b) PAni/PTSA – MWNT Composite (Ethanol)*

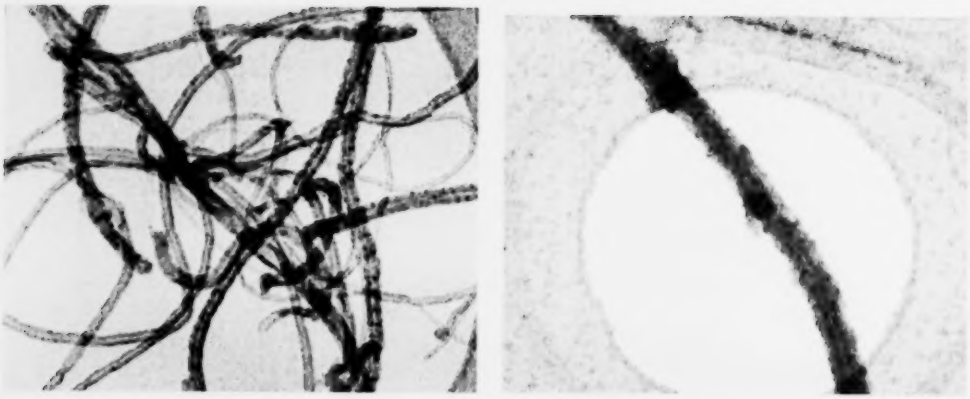


Figure 4. *TEM images of a) MWNT (as received), and b) PAni/PTSA – MWNT Composite (Ethanol)*

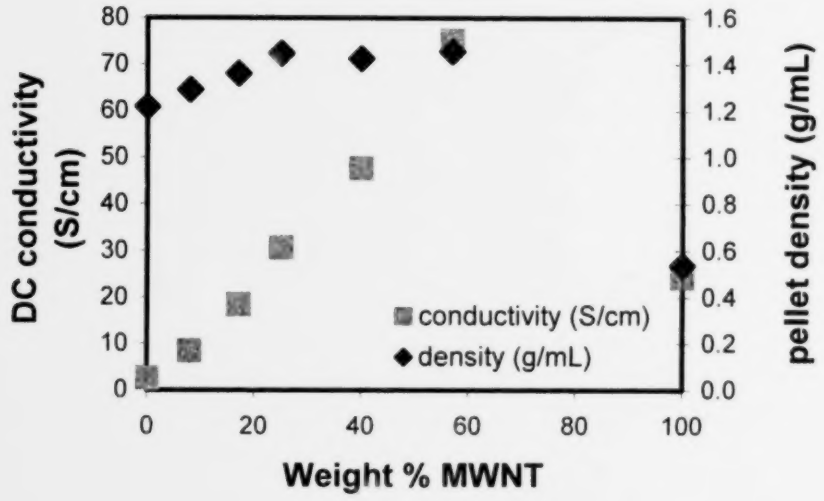


Figure 5. *A Plot of Composite DC Conductivity and Density Versus Weight % MWNT in PAni/PTSA – MWNT Composites (Ethanol)*

3.1.2 PAni/PTSA-CNF (in ethanol)

Using a method similar to that of the carbon nanotubes, carbon nanofibers were dispersed in ethanol, and polyaniline was prepared in the carbon dispersion. Figure 6 illustrates TEM images of the as-received CNF and the PANi-CNF composite. The as-received CNF are obviously much larger than the carbon nanotubes, and appear to be much more rigid. In addition TEM diffraction contrast effects are also observed (highly graphitic). The TEM image of the composite indicates that most of the nanofibers exhibit a rough coating, with some PAni particles adhered to the surface.

The conductivity of pressed pellets of the PAni-CNF composites, as measured by the four-point probe method, was found to increase with increasing CNF content (see Figure 7). This is consistent with the PAni-CNT trend. A notable difference between the nanotubes and nanofibers, is that the nanofibers exhibit a lower conductivity than the polyaniline, thus even at the lowest nanofibre loading investigated (15 wt %), the composite already exhibits higher conductivity than the components alone. This apparent conductivity enhancement is likely due to a more efficient electrical network, as discussed above.

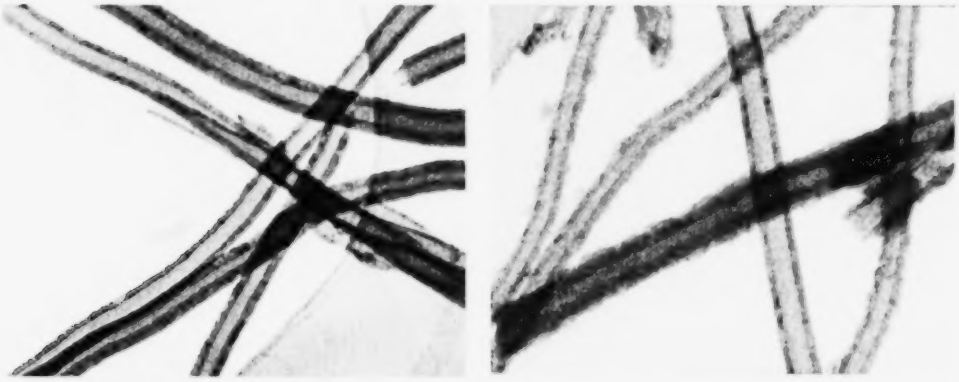


Figure 6. *TEM images of a) Carbon Nanofibres (as received), and b) PAni/PTSA – Carbon Nanofibre Composite (Ethanol)*

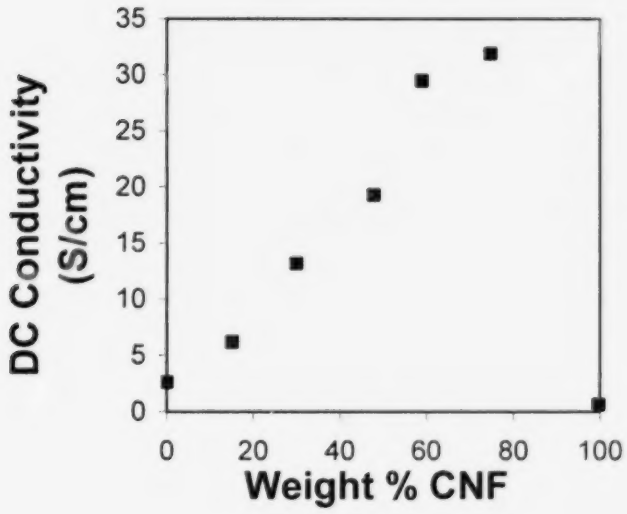


Figure 7. *A Plot of Composite DC Conductivity Versus Weight % Carbon Nanofibre in PAni/PTSA – CNF Composites*

3.2 PAni/DBSA Carbon Nanostructures

3.2.1 PAni/DBSA-MWNT

3.2.1.1 PAni/DBSA-MWNT (in toluene)

By SEM, the polyaniline coating in PAni/DBSA-MWNT composites is barely discernible (see Figure 8). In fact the coating is so thin it is hardly visible by TEM (see Figure 9), although the presence of polyaniline bridging neighbouring nanotubes is readily observed. Despite the extremely thin coating, DC conductivity measurements of PAni/DBSA-MWNT indicate the presence of a conductivity enhancement despite the fairly low DBSA concentration (0.03 M), and thus the lower doping level of the polyaniline. Such a low DBSA concentration was used as it was found to disperse the nanotubes better than higher concentrations.

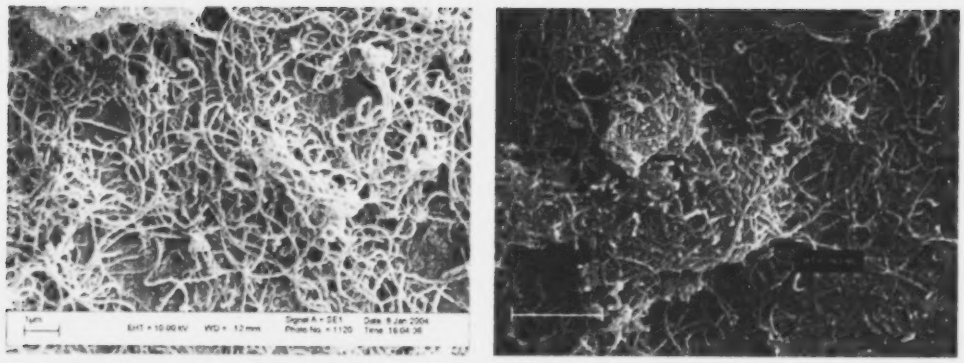


Figure 8. *SEM images of a) MWNT (as received), and b) PAni/DBSA – MWNT Composite (Toluene)*

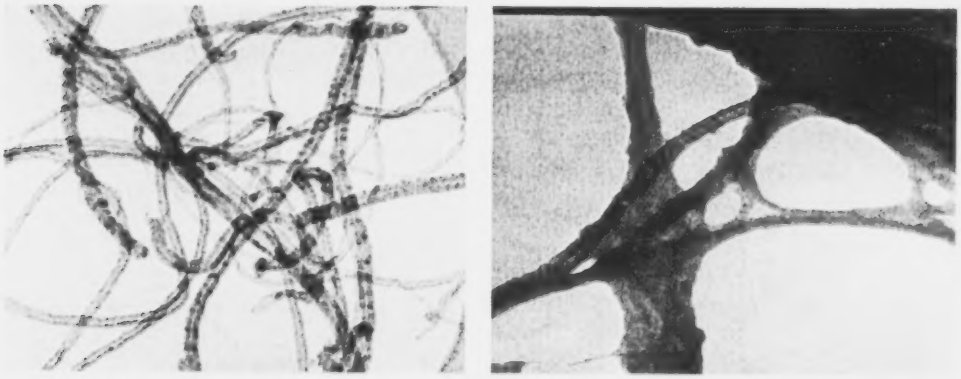


Figure 9. *TEM images of a) MWNT (as received), and b) PAni/PTSA – MWNT Composite (Toluene)*

3.2.1.2 PAni/DBSA-MWNT (in ethanol)

Since ethanol as a medium seemed to result in larger degree of coating, experiments were performed in ethanol, with some interesting results. SEM images of the PAni/DBSA-MWNT composites prepared in ethanol indicate the presence of non-uniformly coated tubes, uncoated tubes, as well as tubules and ribbons (which appear to be large collapsed tubules) (see Figure 10). The latter species were found to be significantly larger than the nanotube species, on the order of several hundred nanometers, and are believed to arise from the formation of columnar micelles of anilinium dodecylbenzenesulfonate, which are insoluble in ethanol. These same structures were observed in the absence of carbon nanotubes. Further investigation into the nature of the tubules and ribbons is underway.

Figure 10. *SEM images of a) MWNT (as received), and b) PAni/DBSA – MWNT Composite (Ethanol)*

3.2.2 PAni/DBSA-CNF (in toluene)

Similar results were obtained for polyaniline – carbon nanofibre composites prepared in toluene, with DBSA as the dopant (see Figure 11). The composite conductivity exceeds that of each component individually when the nanofibre loading reaches ~ 30 weight %, although this likely occurs at loadings between 20 and 30 weight %. This conductivity enhancement is believed to result from the formation of a more efficient electrical network, as previously discussed.

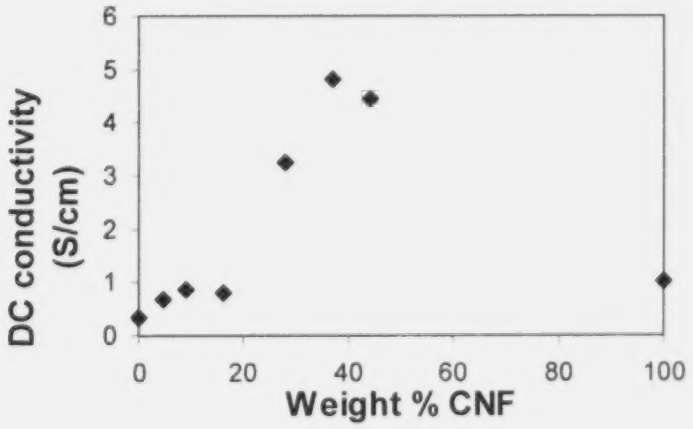


Figure 11. *A Plot of Composite DC Conductivity Versus Weight % Carbon Nanofibre in PAni-DBSA – CNF Composites (Toluene)*

4. Conclusions

Although these are preliminary results, there is much promise regarding *in-situ* polymerization as a means of coating carbon nanotubes and carbon nanofibres with conducting polymers. The results indicate the presence of a polyaniline coating, although it is not uniform and contains polyaniline particles, and the conductivity data indicate that electronic interaction between the polyaniline and carbon nanostructures exists. Electron microscopy images of composites prepared in ethanol clearly show that the polyaniline coats both MWNT and CNF very well (for both PTSA and DBSA). The coating is observed to be fairly rough in texture, and quite thick as a result of the insolubility of polyaniline in ethanol. For composites prepared in toluene (in which PAni/DBSA is fairly soluble), the coating is quite thin and not readily observed by SEM, however TEM images indicate the presence of a thin coating, as well as the existence of polyaniline spanning the nanotubes.

DC conductivity data show an increase in conductivity with MWNT or CNF content, over and above the bulk carbon nanostructure conductivity. The enhancement in conductivity may be attributed to (at least) two factors: the reduction in contact resistance between the nanotubes or nanofibres as a result of the conductive polymer on and between the carbon (more efficient network resulting from reduced contact resistance), and increased packing efficiency (as observed by the density). In addition, the nanostructure surface may have a templating effect on the formation of the polyaniline such that a more ordered polymer results; such an effect may serve to improve conductivity by increasing charge mobility.

Given the promise of these preliminary results, there is significant experimental work required to properly follow up these results. Initially, replication of many of these experiments is necessary, as some of the conductivity data represent single experiments. Although a trend is certainly evident, reproducibility is critical to ensure data accuracy. In terms of fabrication of the composites, there are a number of areas that should be further investigated to ensure optimal composite formation: optimal dispersion of the nanostructures prior to polymerization needs to be ensured, surface functionality of the starting carbon nanostructures needs to be assessed, the conditions for producing a controllable, uniform polymer coating need to be optimized and the coating needs to be accurately measured (using high resolution transmission electron microscopy, HRTEM), interaction between polymer and nanostructures needs to be assessed spectroscopically, and lastly, depending on the application, the polymer – nanostructure interaction needs to be optimized (investigate the ramifications of controllably introducing surface functionality and polymeric substituents, for example).

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List of symbols/abbreviations/acronyms/initialisms

APS	ammonium persulfate
CNF	carbon nanofibre(s)
CP	conducting polymer(s)
DBSA	dodecylbenzenesulfonic acid
DC	direct current
DND	Department of National Defence
E_g	band gap
HA	protonic acid
μm	micrometer, or micron
mm	millimeter
MWNT	multi-walled nanotube
PTSA	*p*-toluenesulfonic acid
NSERC	Natural Sciences and Engineering Research Council
NT	nanotube
π	pi
PAni	polyaniline
PTSA	*p*-toluenesulfonic acid
SEM	scanning electron microscope (or microscopy)
SWNT	single-walled nanotube
TEM	transmission electron microscope (or microscopy)

Glossary

Technical term	Explanation of term
band gap (E_g)	The energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO)
conjugated π system	A system of alternating single and double bonds.
π electrons	Electrons occupying a conjugated π system.

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(U) Les nouveaux matériaux possédant des propriétés électroniques intéressantes, comme les nanotubes de carbone et les polymères conducteurs, suscitent un intérêt considérable. À cause de propriétés exceptionnelles et la facilité avec laquelle on peut les adapter à différents usages, ces deux familles de matériaux récemment découvertes ont attiré l'attention de la communauté des chercheurs. On retient particulièrement la possibilité de produire, en combinant ces deux espèces, un composite aux propriétés qui leur seraient supérieures, notamment les propriétés électriques résultant de la synergie. Nous avons élaboré, sous diverses conditions de réaction, des composites de nanotubes de carbone et de polyaniline, ainsi que de nanofibres de carbone et de polyaniline, et nous avons caractérisé leur conductivité en courant continu et par microscopie électronique (en transmission et par balayage). Nous présentons les résultats de nos premières expériences.

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